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The use of tristimulus colorimetry for the determination of hydrogen cyanide in air by a modified König method

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Abstract: A simple visual and tristimulus colorimetric method (three-dimensional system CIE-L*a*b*) for the determination of trace amounts of hydrogen cyanide in air has been developed. The method is based on the suction of hydrogen cyanide through a chlorinating cartridge where cyanogen chloride is formed, which is further driven to an indicator disc made of a modified cotton fabric. This indicator disc is placed into an adapter. Prior to analysis, the disc is saturated with a chromogenic reagent, a solution of 5,5-dimethyl-1,3-cyclohexanedione (dimedone) and 4-benzylpyridine in ethanol. In the presence of hydrogen cyanide (cyanogen chloride), a pink coloration emerges on the indicator disc, the intensity of which is evaluated either visually or by use of a tristimulus colorimeter. The detection limit is 0.1 mg m⁻³. The method is mainly suitable for mobile field analyses. It was applied for the CHP-5 chemical agent detector introduced into the equipment of the Czech Army corps.

Keywords: atmosphere analysis; hydrogen cyanide; cyanogen chloride; 4-benzylpyridine; dimedone; tristimulus colorimetry.

INTRODUCTION

Hydrogen cyanide (HCN), with an accent to its structural simplicity, ranks among the very important and remarkable chemicals. It is abundant in nature as a part of plant cyanogenic hetero-glycosides. It is essential in organic cyano chemistry, as an effective pesticide in agriculture, in gold and precious metal mining, or in galvanotechnology. It is formed when various materials, mainly synthetic polymeric materials, burn. In the past, it was produced and used as a chemical weapon and misused as a technical instrument of genocide. Its possible role in chemical terrorism has also been a point of discussion for a long time. Given the relative availability and high toxicity of HCN, it is not surprising that extraor-

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dinary attention is dedicated to its analysis throughout the world. So much the more that from the view of how quickly its effects commence to appear, it presents an unequalled poison inhalation hazard.¹ The exposure limit for HCN has been determined and recommended by the National Institute for Occupational Safety and Health (NIOSH) as 5 mg m⁻³.

The bibliography concerning the analysis of HCN and cyanides is extremely extensive. It comprises a large number of publications dedicated to methods of classic volumetric analysis, electrometric and electrochemical methods, separation methods with an emphasis on chromatographic or optical methods such as spectrophotometry and luminescent analysis. In addition to instrumentally demanding methods, simple methods and means of chemical analysis are also used, which are generally based on an appropriate colour reaction. These on-site analysis methods include, *e.g.*, detection papers, testing strips, tablets, powder, chalks, or detection tubes.^{2,3} The predisposition of HCN dispositions to all kinds of colour reactions is well known and frequently used in practice for air analysis. Evidently, the most widespread is the highly sensitive and selective method of HCN conversion to halogenocyanides, which react with pyridine and its derivatives to form glutacon dialdehyde, which condenses with a series of amines and substances containing active hydrogen as a passive component to give polymethine dyes.⁴ This König reaction was employed for HCN detection in air in numerous modifications, *e.g.*, for sensitive detection crayons⁵ or tubes.⁶ Other methods are based on the reaction of HCN with Cu²⁺ and aromatic amines,⁷ sodium picrate,⁸ *p*-nitrobenzaldehyde,⁹ ninhydrin,¹⁰ aromatic disulphides,¹¹ and on other reactions.

In this paper, a simple and sensitive method for the determination of HCN in the air using tristimulus colorimetry is reported. The method has recently also found application in industry for controlling surface quality and in analytical chemistry.^{12,13} Previously, tristimulus colorimetry was applied in the development of simple methods for the determination of chlorine,¹⁴ sulphur dioxide,¹⁵ formaldehyde¹⁶ and diphosgene.¹⁷ The new method devised for the HCN determination consists in the conversion of HCN to cyanogen chloride (CICN), which reacts with modified König reagent (4-benzylpyridine, dimedone) to give the corresponding polymethine dye (Fig. 1). The conversion to CICN occurs in a chlorinating cartridge. The reaction with a chromogenic agent occurs on the indicator disc inserted into an adapter. After taking an air sample, a characteristic coloration emerges on the disc, the intensity of which is measured using a tristimulus colorimeter or assessed visually.

EXPERIMENTAL

Chemicals and equipment

Potassium cyanide p.a. (Lachema, Czech Republic) served as a standard. Dimedone, or 5,5-dimethyl-1,3-cyclohexanedione, 4-benzylpyridine (both Sigma-Aldrich) and absolute etha-

nol (Riedel de Haen) were used for the preparation of the chromogenic reagent. The basic variant of the chromogenic reagent contained 1.5 g of 5,5-dimethyl-1,3-cyclohexanedione and 10 ml of 4-benzylpyridine in 100 ml of ethanol solution.

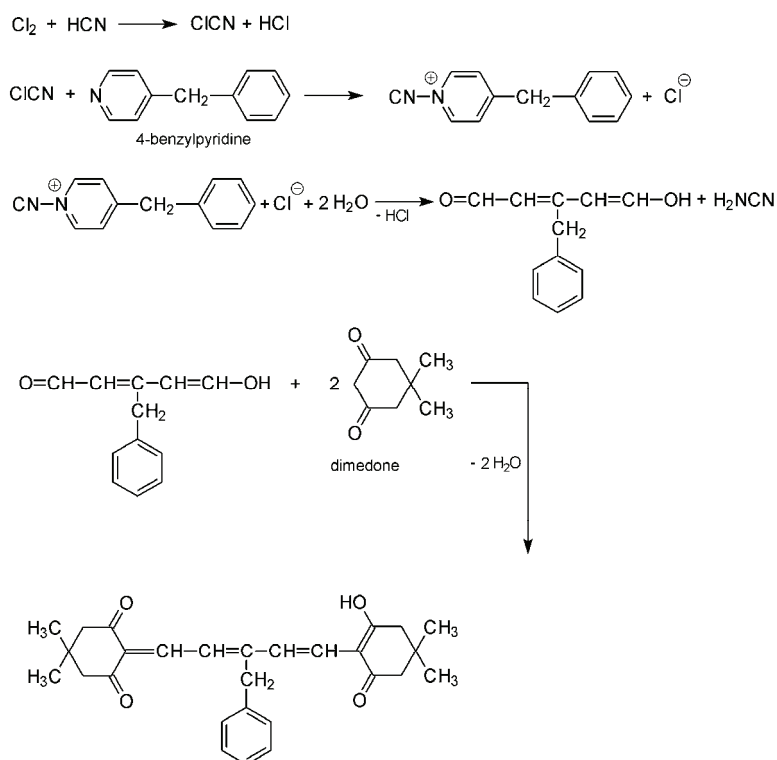


Fig. 1. Mechanism of the analytical reaction.¹⁸

HCN samples were prepared in a test chamber of 712 dm³ volume, equipped with a thermostat (Lamon, Czech Republic). HCN samples were taken using an XDS-10C vacuum pump (BOC Edwards, Great Britain) with an attached flow meter and a CHP-5 chemical agent detector equipped with an electric pump (Oritest, Czech Republic). A portable tristimulus colorimeter LMG-173 (Lange, Germany) was used to measure the coloration intensity. A Helios- α UV/Vis spectrophotometer (Herma Electron, Great Britain) was used to measure the colouring of solutions (HCN concentration control).

Preparation of the indicator disc

The fabric based on a web of cotton threads 0.31–0.33 mm thick was used for the indicator disc. This cotton fabric was impregnated with a solution containing 0.30 g of Na₂B₄O₇·10 H₂O, 0.45 g of H₃BO₃, 0.1 g of NaCl, 2.5 g of silica gel (fraction up to 5 μ m), and 3.0 g of dextran per 100 ml of water. The impregnated fabric was dried freely in the air. Drying was completed in a desiccator above solid sodium hydroxide. After drying, it was formed in a shape of circle with 45 mm in diameter.

Preparation of the chlorinating cartridge

The chlorinating cartridge contained activated silica gel (purified with hydrochloric acid and dried at 150 °C), which was impregnated with an aqueous solution of 5 % sodium carbonate and 2 % monochloramine B. 100 ml of solution was used for 100 g of silica gel. After impregnation, the charge was dried at 80 °C to constant weight. The thus prepared charge was poured into glass tubing with an inner diameter of 5 mm and anchored against motion by polyethylene distributing pieces. The standard length of the layer was 10 mm. The chlorinating cartridge was hermetically sealed to permit long-term storage.

Sample preparation

Various concentrations of HCN were prepared in a test chamber by heating potassium cyanide solution acidified with H_3PO_4 . The actual HCN concentration was determined by a spectrophotometric method. The HCN vapours were pumped from the test chamber by vacuum pump at a rate of $1.0 \text{ dm}^3 \text{ min}^{-1}$ and absorbed for a period of 10 min in an absorption apparatus containing 10 ml of 0.10 M NaOH. To 1 ml of absorption solution with HCN, 1.0 ml of HCl, 1.0 ml of chromogenic reagent (1 % barbituric acid in a mixture pyridine–water 10:90), and 0.5 ml of 0.10 % calcium hypochlorite were added and made up to 5 ml with water. After 30 min, the absorbancy of the solution was measured at 581 nm.

The HCN determination procedure by the devised method

The indicator disc was inserted into an adapter with a supply hose connected to the chlorinating cartridge and a device for regulated intake of air. 50 μl of the chromogenic reagent was dosed to the middle of the indicator disc. Then contaminated air was sucked through the system (at a defined flow rate and suction time). After the sampling, the intensity of the colour stain of about 20 mm in diameter was assessed both visually and using a tristimulus colorimeter. The apparatus for the determination of the HCN concentration in the air using the CHP-5 chemical agent detector (electrical pump) is shown in Fig. 2.



Fig. 2. Apparatus photo: CHP-5 with indicator disc and adapter (a); CHP-5 with indicator disc, chlorinating cartridge and adapter (b).

Tristimulus colorimetry

Tristimulus colorimetry is a type of reflectance colorimetry (spectrophotometry) based on the CIE- $L^*a^*b^*$ colour system.²¹ In this system, L^* represents the neutral axis of brightness, a^* is the chromatic green–red axis ($+a^*$ red, $-a^*$ green) and b^* is the chromatic blue–yellow axis ($+b^*$ yellow, $-b^*$ blue). In practice, the colour difference, ΔE , is also used, which is defined by the equation:

$$\Delta E = [(\Delta L^*)^2 + (\Delta a^*)^2 + (\Delta b^*)^2]^{1/2}$$

where ΔL^* , Δa^* , and Δb^* are the differences between the obtained values of L^* , a^* and b^* for the standard and for the controlled colours. All these parameters can be used as analytical signals, which enable the course of a colour chemical reaction to be quantified. The colour differences (ΔE) can also be assessed according to Table I.

TABLE I. Evaluation of colour differences (ΔE) – utilisation in the polygraphic industry

Difference ΔE	Visual assessment of colour difference
Below 0.2	Unperceivable
0.2–0.5	Very slight
0.5–1.5	Slight
1.5–3.0	Distinct
3.0–6.0	Very distinct
6.0–12.0	Strong
Above 12.0	Very strong

RESULTS AND DISCUSSION

Colour stability

The passage of HCN-contaminated air practically instantaneously induces a pink coloration on the cotton disc, which can be characterised by a reflection curve (Fig. 3). After the sampling, this coloration remains relatively stable for 10 min minimally. The development of all components of the colour system (parameters ΔE , ΔL^* , Δa^* and Δb^*) for this period are documented in Table II.

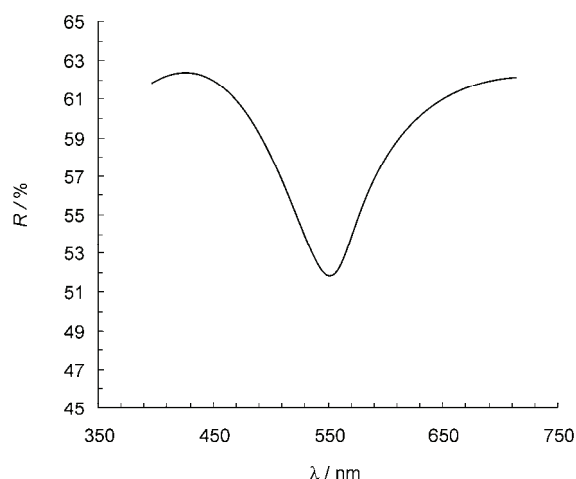


Fig. 3. Dependence of the reflection factor R on the wavelength λ .

Effect of the sampling period

The intensity of stains coloration on the indicator disc is dependent on the volume of the analysed sample (exposition time). The maximum values of the ΔE , ΔL^* , Δa^* and Δb^* parameters were obtained 2 min after air in-take; a longer

exposition resulted in a weaker intensity of coloration. This decrease was caused by oxidation effects of the atmospheric oxygen, drying of the indicator disc and gradual exhaustion of the chlorinating cartridge. The dependence of the individual parameters on the time of HCN sample in-take is given in Table III.

TABLE II. Colour stability – dependence of measured values on time (HCN sampling time: 1 min, flow rate: 1 dm³ min⁻¹, HCN concentration: 1.6 mg m⁻³)

Time of measurement, min	ΔE	ΔL^*	Δa^*	Δb^*
Immediately	4.79	0.72	3.97	-2.58
1	4.15	1.42	3.22	-2.21
2	4.09	1.58	3.07	-2.25
4	3.84	1.74	2.74	-2.05
6	3.73	1.94	2.50	-2.00
8	3.59	2.08	2.27	-1.84
10	3.53	2.25	2.08	-1.75

TABLE III. Dependence on exposure time (of HCN sampling)

Time of sampling, min	ΔE	ΔL^*	Δa^*	Δb^*
1	9.02	-4.91	6.69	-3.53
2	15.16	-6.89	12.08	-6.02
3	14.28	-6.72	11.56	-5.01
4	12.87	-6.39	10.11	-4.76

Effect of the sampling flow rate

The dependence of monitored parameters on the flow rate of contaminated air is given in Table IV. It is evident that the values of the analytic signals decrease with increasing flow rate. This is probably caused by different periods of contact of the sorption layer of the indicator disc with HCN.

TABLE IV. Dependence on air flow rate (HCN concentration: 1.6 mg m⁻³, suction time: 1 min)

Flow rate, dm ³ min ⁻¹	ΔE	ΔL^*	Δa^*	Δb^*
0.5	6.37	-0.07	5.17	-3.72
1.0	4.79	0.72	3.97	-2.58
2.0	4.52	0.18	3.92	-2.25
3.0	4.32	0.25	3.74	-2.16

Effect of reagent composition and chlorinating cartridge capacity

The dependence of colour response on the composition (concentration) of chromogenic reagent is given in Table V. Any higher concentration of reagent has a demonstrable effect on the potency to capture HCN on the indicator disc and results in an increased sensitivity of the determination.

On the contrary, with higher capacity (length of layer) of the chlorinating cartridge, the sensitivity of the HCN determination decreases as shown in Table

VI. On the other hand, a higher capacity may result in a prolonged effective life of the chlorinating cartridge and improved determination selectivity.

TABLE V. Dependence on reagent composition (A – basic variant reagent, see experimental section, B – twice-diluted reagent, C – twice-concentrated reagent)

Reagent concentration	ΔE	ΔL^*	Δa^*	Δb^*
A	4.79	0.72	3.97	-2.58
B	4.44	0.54	3.58	-2.58
C	8.90	4.50	8.84	-5.58

TABLE VI. Dependence on length of chlorinating cartridge

Cartridge length, mm	ΔE	ΔL^*	Δa^*	Δb^*
10	12.52	-2.79	9.41	-7.77
20	12.46	-2.07	9.02	-8.35
40	8.16	-0.16	5.42	-6.10

Interference

The analytical method based on the conversion of HCN to ClCN, which gives a characteristically coloured polymethine dye with 4-benzylpyridine and dimedone, is highly selective. Only ClCN or BrCN gave results comparable to those of HCN (Table VII). They can be distinguished from HCN performing the detection without insertion of the chlorinating cartridge. Among other interfering substances, a similar pink coloration is produced by phosgene oxime and nitrogen oxides, but at higher concentrations. Chloropicrin gives a yellow-orange coloration. The chemical composition of the chlorinating cartridge ensures the high resistance of this method against the effects of acidic and alkaline pollutants (HCl, SO₂, H₂S, and NH₃). Volatile aldehydes in higher concentrations reduce the sensitivity of the HCN determination because they deplete the chlorinating cartridge.

TABLE VII. Effect of diverse compounds on the detection of 0.40 mg m⁻³ HCN

Compound	Colour	Tolerance limit (visually), mg m ⁻³
Cyanogen chloride	Pink	0.4
Cyanogen bromide	Pink	0.8
Phosgene oxime	Pink	5
Chloropicrin	Yellow	20
Nitrogen dioxide	Pink	50
Hydrogen sulphide	No colour	100
Ammonia	No colour	100
Hydrogen chloride	No colour	200
Sulphur dioxide	No colour	200
Acetonitrile	No colour	200
Benzaldehyde	No colour	200

Calibration graph

The calibration graph for the determination of HCN is shown in Fig. 4. The HCN detection limit attained by the tristimulus colorimeter was 0.10 mg m^{-3} . For the visual method, the HCN detection limit (threshold perception) was 0.40 mg m^{-3} . For visual assessment, it is advisable to compare the intensity of the colour stain with a reference standard representing a colour scale $0\text{--}10 \text{ mg m}^{-3}$ with a 0.2 mg m^{-3} resolution.

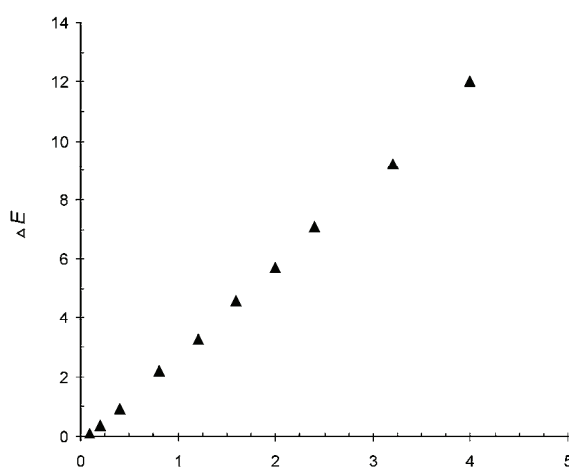


Fig. 4. Calibration graph. Dependence of ΔE on HCN concentration (flow of $1.0 \text{ dm}^3 \text{ min}^{-1}$, 1 min exposure). Calibration line equation: $y = 2.9249x$, $R^2 = 0.9971$.

The reproducibility of test results for 0.10 , 1.0 and 5.0 mg m^{-3} concentrations show that the relative standard deviation of the response (ΔE) ranged from 12 to 17 %.

Application

The elaborated visual and tristimulus colorimetric method for HCN determination can be applied to many different areas of field analysis – military, Industrial disaster recovery, and environment control. The method was devised for application of a CHP-5 chemical agent detector introduced into the equipment of the Chemical Corps of the Czech Army (Fig. 2). The standard airflow rate through this apparatus is $1.0 \text{ dm}^3 \text{ min}^{-1}$, the suction time is 1 min. Results of HCN determination by the proposed method and of a comparable method are presented in Table VIII. When stored in hermetically sealed containers, the indicator disc can be used for several years. Solutions of the chromogenic reagents are stable; the standard variant showed stability for at least 12 months. The effective life of a closed chlorinating cartridge is several years. When opened, it can be used repeatedly until the charge is exhausted.

Using the devised tristimulus colorimetric method, trace concentrations of HCN in the atmosphere can be proved. As shown in Table IX, the detection limit

is comparable to, and even lower, than those of any known methods and technical means of HCN detection. The developed analysis procedure has universal application, which means that it enables the application of other liquid chromogenic reagents to determine a whole range of toxic substances in air.

TABLE VIII. Determination of HCN in air by the developed and a reported method (detector tube, tristimulus colorimetry)⁶

HCN added mg m ⁻³	HCN found by developed method mg m ⁻³	HCN found by reported method mg m ⁻³
1.2	0.9	1.0
2.4	2.1	2.2
3.6	3.2	3.3
4.8	4.3	4.5

TABLE IX. Comparison with technical means of HCN detection

Name	Principle	Detection limit, mg m ⁻³	Ref.
M256, USA	Indicator paper, colorimetry	9.0	19
HCN-2 Auer, Germany	Detection tube, colorimetry	2.2	20
CMS Dräger, Germany	Chip measurement system, optical sensor	2.2	21
Indicator tape, Japan	Reflectance spectrophotometry	0.2	7
Bruker A2, Germany	Electrochemical sensor	50.0	19
RAID-1, Germany	Ion mobility spectrometry (IMS)	2.2	19
Developed method	Indicator disc, tristimulus colorimetry	0.1	–

ИЗВОД

ПРИМЕНА ТРИСТИМУЛУС КОЛОРИМЕТРИЈЕ ЗА ОДРЕЂИВАЊЕ ЦИЈАНОВОДОНИКА У ВАЗДУХУ МОДИФИКОВАНОМ KÖNIG МЕТОДОМ

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Развијена је једноставна тристимулус колориметријска метода (тродимензионални систем СТЕ-*L*a*b**) за одређивање цијановодоника у ваздуху. Метода се заснива на сукцији цијановодоника кроз хлоровани кертриц у коме се формира дицијан, који се даље спроводи до индикаторског диска од модификоване памучне тканине. Индикаторски диск је смештен у адаптеру. Пре анализе диск се засити хромогеним реагенсом, раствором 5,5-диметил-1,3-циклохександионом (димедон) и 4-бензилпиридином у етанолу. У присуству дицијана индикаторски диск се обоји љубичасто, а интензитет обојења се може проценити било визуелно било употребом тристимулус колориметрије. Граница детекције износи 0,1 mg m⁻³. Метода је погодна углавном за теренске анализе и нашла је примену за детекцију хемијског агенса СНР-5 у војсци Чешке Републике.

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